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<p>(21) International Application Number: PCT/EP93/02346 (22) International Filing Date: 30 August 1993 (30.08.93)</p> <p>(30) Priority data: S922758 21 October 1992 (21.10.92) IE</p> <p>(71) Applicant (<i>for all designated States except US</i>): GAIT PRODUCTS LIMITED [GB/GB]; 14D Athol Street, Douglas, Isle of Man (GB).</p> <p>(72) Inventor; and (75) Inventor/Applicant (<i>for US only</i>) : KRISTIANSEN, Kas-tholm [DK/DK]; Mareakvej 12, DK-6700 Esbjerj (DK).</p> <p>(74) Agents: McKEOWN, Yvonne, Mary et al.; MacLachlan & Donaldson, 47 Merrion Square, Dublin 2 (IE).</p>		<p>(81) Designated States: BR, CA, NO, RU, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i></p> <p>102(b) 1, 2, 3, 5, 6 9, 10, 25 - 26, 34, 35, 37, 38 - 41 53, 54, 57</p>																																									
<p>(54) Title: COMPOSITION FOR USE IN WELL DRILLING AND MAINTENANCE</p> <p style="text-align: center;">KCL-CITRIC ACID PERFORMANCE VS CONCENTRATIONS</p> <table border="1"><caption>Data points estimated from the graph</caption><thead><tr><th>Concentration (g/l)</th><th>Performance (g/l)</th><th>KCL Concentration (g/l)</th><th>Citric Acid Concentration (g/l)</th></tr></thead><tbody><tr><td>0</td><td>~250</td><td>~25</td><td>~50</td></tr><tr><td>50</td><td>~300</td><td>~50</td><td>~100</td></tr><tr><td>100</td><td>~320</td><td>~100</td><td>~150</td></tr><tr><td>150</td><td>~330</td><td>~150</td><td>~200</td></tr><tr><td>200</td><td>~340</td><td>~200</td><td>~250</td></tr><tr><td>250</td><td>~350</td><td>~250</td><td>~300</td></tr><tr><td>300</td><td>~360</td><td>~300</td><td>~350</td></tr><tr><td>350</td><td>~370</td><td>~350</td><td>~400</td></tr><tr><td>400</td><td>~370</td><td>~400</td><td>~450</td></tr></tbody></table>				Concentration (g/l)	Performance (g/l)	KCL Concentration (g/l)	Citric Acid Concentration (g/l)	0	~250	~25	~50	50	~300	~50	~100	100	~320	~100	~150	150	~330	~150	~200	200	~340	~200	~250	250	~350	~250	~300	300	~360	~300	~350	350	~370	~350	~400	400	~370	~400	~450
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<p>(57) Abstract</p> <p>A composition for dissolving filtercake deposits left by drilling mud in well bores comprises an aqueous solution of a water soluble organic acid and a salt selected from alkali metal chloride, alkali metal formate, acid tetraphosphate, alkaline earth chloride or alkali metal thiophosphate. Each of the acid and salt are present in the range of 0.5 % to 75 % w/w of the composition. The preferred acid is citric acid and the preferred salt is potassium chloride. The composition is useful as an additive for freeing stuck pipe in well bores and as a fixer spacer for cementing pipe in well bores. A further use of the composition is as well a stimulation fluid in oil and gas production wells, where the composition is effective to dissolve filtercake which blocks pores in the production formation.</p>																																											

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COMPOSITION FOR USE IN WELL DRILLING AND MAINTENANCE

The present invention relates to a composition for use in the drilling and maintenance of wells, particularly oil and
5 gas wells.

In the drilling of oil, gas, water, condensate, geothermal, mineral coring or any other type of well requiring a rotary drilling rig, drilling fluid is introduced into the
10 descending bore formed by the drill head. The drilling fluid serves to lubricate the bore and drill head. The drilling fluid, which is commonly referred to as drilling mud, deposits a lining on the walls of the bore, the lining being comprised of the solid components of the drilling
15 mud. This deposited lining is known as filtercake.

A frequently encountered problem in drilling wells, both onshore and offshore, is that the pipe which is introduced into the bore as the drilling proceeds tends to adhere to
20 the filtercake. To overcome this problem, it is necessary to pump chemicals known as "stuck pipe additives" into the bore to lubricate the bore sufficiently to free the pipe from the filtercake.

25 Unfortunately, the stuck pipe additives themselves raise an additional problem. Most stuck pipe additives are petroleum based surfactants which need to be blended with an oil in order to carry out their function effectively. Accordingly, environmental concerns have led to the
30 outright banning of these substances or to the regulation of their use under stringent and expensive control criteria.

When a well bore has been completed and has been lined with

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piping, for example steel casing, the next step is that the casing is fixed to the walls of the bore by cement. The presence of the filtercake lining the bore raises another difficulty at this stage, as it decreases the efficiency of
5 the bonding between the bore wall, cement and casing.

Yet another disadvantage of the presence of drilling mud in the bore is that filtercake residues can block the pores in a subterranean formation through which oil or gas flow
10 into the bore, resulting in inefficient production from that well.

Attempts have been made to solve the problems caused by filtercake deposits in wells by flushing acid mud into the
15 bore to dissolve the filtercake. However, as the acids generally used up to now have been strong acids such as hydrochloric acid, these attempts are largely unacceptable as they lead to danger of severe acid burns to personnel in addition to raising the further environmental hazards
20 associated with the disposal of the acid mud after use into marine, freshwater or land environments.

US-A-4609475 in the name of Halliburton Company discloses an aqueous composition for removing polymeric materials
25 from a subterranean formation. The composition includes a water soluble carboxylic acid such as citric acid, and an alkali metal salt as an oxidising agent. In GB-1494448 in the name of Shell Internationale Research Maatschappij B.V., there is described an aqueous solution including a
30 weak acid for acidizing subterranean formations. The solution includes a fluoride salt, a weak acid and a weak acid salt to lower hydrogen fluoride concentration, thereby to avoid the reaction of acid with carbonates to form precipitates. The acid may be citric acid and the salt may

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be sodium, potassium or ammonium acetate, formate or citrate. A similar disclosure is made in GB-1495841, also in the name of Shell International Research Maatschappij B.V., with the omission of the fluoride salt from the
5 solution.

GB-A-2174435 in the name of Amerigo Technology Limited (Canada) discloses means for improving recovery from a well by flushing in a strong acid, followed by a solution of an
10 acid such as citric acid, a surfactant and a clay stabilizer. Use is made of potassium chloride as the clay stabilizer.

It is an object of the present invention to overcome the
15 listed disadvantages associated with the use of drilling mud by providing a clean, inexpensive and environmentally acceptable composition for breaking down filtercake deposits in well bores.

20 Accordingly the present invention provides a composition effective to dissolve filtercake in a well bore, the composition comprising one or more water soluble organic acids in an aqueous solution of one or more of a salt selected from alkali metal chloride, alkali metal formate,
25 acid tetraphosphate, alkaline earth chloride, alkali metal thiosulphate or the like.

The present invention also provides a dry powder mixture for use in the preparation of an aqueous composition which
30 is effective to dissolve filtercake in a well bore, the mixture comprising a salt of one or more water soluble organic acids and one or more of a salt selected from alkali metal chloride, alkali metal formate, acid tetraphosphate, alkaline earth chloride, alkali metal

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thiosulphate or the like.

The constituents of the composition may conveniently be supplied as a dry powder mixture, with instructions given 5 as to how the powder should be reconstituted in the field for use. Supply of the material in dry form is more economical for the manufacturer, whose packaging, transport and other costs will be lower than for supply of the aqueous composition.

10

Conveniently, the water soluble acid comprises 0.5% to 75% w/w of the composition, and preferably 10% to 35%.

Ideally, the salt comprises 0.5% to 75% w/w of the composition; and preferably 10% to 35%. In a preferred 15 embodiment, the water soluble organic acid is selected from the group comprising citric acid, oxalic acid, ascorbic acid, succinic acid, malonic acid, maleic acid and lactic acid, or any combination thereof, in any ratio, and the salt is selected from the group comprising 20 potassium chloride, sodium chloride, magnesium chloride, sodium acid tetraphosphate, sodium thiosulphate pentahydrate, sodium formate, potassium formate and cesium formate, or any combination thereof, in any ratio.

25 The composition conveniently includes an alkali metal pyrophosphate salt, preferably sodium acid pyrophosphate. The most preferred embodiment comprises 200 to 230g citric acid monohydrate and 200 to 235g potassium chloride per litre of water and preferably further includes 15 to 25g 30 sodium acid pyrophosphate per litre of water.

The invention further provides the uses of the above composition as (1) a filtercake dissolving additive in the drilling and maintenance of wells, (2) a fixer spacer in

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the drilling of wells, and (3) a stimulating fluid for blocked or partially blocked oil or gas wells.

The composition according to the invention dehydrates clay
5 particles in the drilling fluid filtercake. It further solubilises any entrained carbonates in the filtercake, thereby destroying the matrix integrity that binds the filtercake together. Polymers in the filtercake are destroyed by acid hydrolysis thereby further solubilising
10 the filtercake components. Thus, the effect of the composition of the present invention is to solubilise filtercake, after which the non-toxic aqueous composition containing filtercake residue can be flushed from the bore and disposed of without causing any particular
15 environmental hazard.

The invention further provides a method of freeing stuck pipes in the drilling of well bores, the method comprising introducing a composition of the invention as described
20 above into the bore in the region of the stuck pipe so as to dissolve and remove filtercake adhering to the pipe. The method is very simple to use and is completely safe for personnel as the composition contains only non-hazardous components, citric acid and other organic acids being mild
25 acids and potassium chloride being an innocuous salt. Citric acid has formerly been used in well-drilling applications on a very limited scale for lowering the pH of drilling mud. Potassium chloride has been used in small quantities to inhibit the swelling of drilling mud by water
30 absorption. The use of these two components in aqueous solution as a solvent for filtercake has never been heretofore suspected or recognised.

The invention still further provides a composition as

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described above for use as a fixer spacer in the drilling of wells. As referred to above, the presence of filter cake deposits on the walls of the bore and pipes often results in poor cement adhesion of the pipe into the well.

5 This problem can be overcome by using the composition of the invention as a spacer between the pipe and the bore walls. Once pumped in, the composition will dissolve the filtercake from the surfaces to be fixed by a fixer compound such as cement or the like, after which the cement
10 can be introduced into the space between the cleaned surfaces. This results in an effective bond of the pipes in the bore.

Accordingly, the invention also provides a method for
15 securely fixing well casing pipe in a well bore, the method comprising introducing the composition of the invention as described above into the space between the pipe and the bore walls, allowing the composition to dissolve filtercake from the said space and introducing a fixer compound to
20 displace the composition and dissolved filtercake residues. The fixer may be cement or any other suitable fixing compound.

25 Yet another application for the inventive composition is its use in the so-called stimulation of wells to free blocked pores. Accordingly the invention provides a composition as described above for use as a stimulating fluid for blocked or partially blocked oil or gas wells. The composition is capable of stimulating oil or gas
30 production from wells by dissolving filtercake from the pores in the sub-stratum through which the oil or gas flows into the well.

The invention further provides a method for stimulating

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production from an oil or gas well, comprising introducing into the well an amount of the composition of the present invention effective to unblock gas or oil supply pores by dissolving blocking filtercake therefrom.

- 5 Although it is well known that at equal concentrations certain cations such as lithium, sodium, potassium, magnesium and calcium, would be more prone to cationic substitution in an argillaceous clay formation in the descending order noted, it has been previously stressed
- 10 that preferential ionic replacement stabilizes these clays. The present invention employs the opposite concept whereby the ionic exchange capacity is brought to and beyond the stage of electrolytic equilibrium. Although the pattern of this isomorphic type substitution will vary greatly with
- 15 mineral types, the composition of the invention is useful with the most common clay, shale and marl types which are carried into the drilling fluid systems as a result of the drilling process, and are a resultant contaminant thereof. These clays, once deposited on drill collars, drill bits,
- 20 other subsurface metal tools, and of course, the well bore itself, have to a great extent reached an equilibrium with the aqueous solution environment. It is thought that the composition acts in two different ways, as described below.

25 1. Clay Destabilisation

The composition employs a near saturation level of dissolved salt, preferably a potassium salt, to provide a highly destabilizing electrolytic environment. The level of cation available is such that the diffuse area near the

- 30 surface of the clay crystals themselves becomes compressed (the thickness of this diffuse area (Gouy layer) is proportional to the concentration of electrolyte present).

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The concentration of electrolyte is such that Born repulsion is overcome. This repulsion, which would normally prevent an interpenetration of the crystal lattices, is overcome forcing the destabilizing results of

5 (a) desorption of water from the faces of the clay and (b) cationic exchange within the clay matrix of the native clay ion (normally sodium or calcium) with the potassium ion.

Although potassium inhibited drilling fluids are
10 occasionally used as clay stabilizers in drilling suitable formations, the cation is provided in a slight excess, rather than in the high concentration which would result in destabilisation. That is to say, the level of potassium in solution is aimed at an "ideal balance" or stabilizing
15 situation and destabilising levels are particularly avoided. As such, in many instances, the level of potassium in the drilling fluid is constantly being consumed but remains in slight excess to provide the raw material for the ion exchange.

20

In contrast, by employing a deliberately destructive level of electrolyte in solution, the composition of the invention forces a physical ionic change in the equilibrium of the filtercake environment. It is well known that the
25 potassium ion, when present in basal exchange sites which are in a dehydrated state, occupies less area than the calcium and magnesium ions which are present in hydrated states. Similarly, potassium ion occupies far less area than the calcium, magnesium or sodium ions in the same clay
30 crystals. This combined with the de-watering, creates fissures, cracks and blisters in the uniform surfaces that have been created in the stable environment. The clay matrix losses its integrity, cohesion and literally and figuratively crumbles.

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2. Acid Dissolution

The inclusion of an acid in the solution aids the dissolution of the filtercake by dissolving the entrained carbonates and polymers. Although well known for this purpose, the use of acid in conjunction with a destructive electrolytic concentration has not heretofore been disclosed. Formerly, attempts at removing bore contaminants have concentrated on the protection of the reservoir through stabilizers. The invention reverses this trend by using the composition of the invention to remove entrained and adsorbed contaminants which result from exposure to the drilling fluid through (a) the destructive use of high electrolytic fluids to crack acid insoluble clay surfaces thereby allowing (b) exposure to the acid solution of carbonates embedded in the filtercake matrix which in turn (c) exposes new clay faces to electrolytic desorption of water and cationic exchange all of which results in (d) the removal of the cracked and shrinking clay particles, and dissolved polymeric remnants by the expanding carbon dioxide gas residues formed in the acidization of the carbonates and polymers.

The inclusion of the acid is viable as it is known that the pH of the fluid does not effect the ion exchange capacity of clays. The validity of the acid inclusion is verified by laboratory tests on many lab and field muds, as exemplified in the Examples, which verify that lab muds containing low levels of raw polymers, high levels of American Petroleum Institute (API) commercial bentonite, and low levels of API commercial barite, are relatively unaffected by the inventive composition, showing only some cracking and blistering and no actual removal of mud. This

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indicates that no carbonate material is available for the gas disruption or solubilization of polymers beneath the surface in the test frame of 60 minutes. The same formulation however taken from a field mud, shows immediate 5 blistering, bubble formation, and filtercake lifting within 30 minutes.

This is due to the fact that unlike under laboratory conditions, actual drilling takes place in circumstances 10 where carbonates and bicarbonates are created (1) through the encounter of CO₂ in the well bore (quite common at all levels), (2) breakdown of mud chemicals used, (3) as secondary by products of bacterial activity, (4) as carbonates from barite and (5) as carbonates from different 15 clays and carbonate formations.

The testing of field muds of all types (excluding oil based muds) using the composition of the invention has verified the above analysis that the destructive oil well chemistry 20 disclosed herein for removing drilled solids and polymeric filtercakes from drilling tools and well bores (stuck pipe), specialized casing steel (cement spacer) and reservoir faces (stimulation cleanup fluid) is useful in the field when drilling carbonate-containing bores. 25 However, it will be appreciated that the applications of the composition and methods of the invention are not limited to oil and gas wells, but that they are equally useful for all types of wells and other drillings in carbonate-containing formations.

30

The application of this destabilizing process to certain reservoirs may be undesirable, particularly where the production zones are interbedded with sensitive clays. In carbonate and sandstone reservoirs, it would be ideal.

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Reservoirs would have to be tested on an individual basis by core flooding to determine the usefulness of the invention at a particular site.

5 The use of formulations of different salts and different organic acids gave varying orders of performance, as exemplified in the Examples given herein. In addition, the criteria for performance are adjustable for safety and toxicity to human and animal/plant species. Different
10 levels of oxalic, maleic and acetic acids with varying doses of sodium, potassium and calcium salts derived poor results. A strongly acidic mixture of acetic acid with calcium chloride or calcium bromide gave no effect on the clay matrixes worth noting.

15 The use of phosphoric acid with potassium tetrephosphate and potassium chloride yielded positive results, but was poorer than the formulation identified as Formulation A in the following Example 2. In addition, the use of
20 phosphoric acid is questionable at the levels required to achieve these results, when regarded from the point of view of safety, and deposition of phosphates into a marine or freshwater environment.

25 Experiments using acidified potassium, sodium and cesium formate were positive. These salts can be utilized for the same applications, albeit at different density requirements and some loss of performance due to their alkaline nature compared to the Formulation A product, as described in
30 Example 2.

Example 1 - Preparation of filtercake samples

In the initial stages of experimentation for filtercake

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removal, a standard American Petroleum Institute (API) filterpress apparatus was used to form the filtercakes.

The methodology entailed placing the relevant mud samples in the liquid chamber of the filtercake apparatus, beneath 5 which has been placed a 7.6 cm (3 inch) circular sheet of Whatman No. 50 filterpaper. The covering was placed over the liquid container vessel and the chamber pressured to 150 psi using gas cartridges, and sustained for 60 minutes. The chamber was then depressurised, and the whole mud 10 decanted. The filter paper with the filtercake was removed, and gently washed with fresh water to remove excess whole mud.

The thickness of the filtercakes was dependent on the mud types, but were on average 0.8 to 1.6 mm (1/32 to 1/16 15 inch) thick. The type of muds tested are as noted in Table 1. All muds were seawater-waterbased muds.

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Sample No.	1	2	3	4	5	
Mud Type	Polymer	Polymer	Polymer	Bentonite	Bentonite	
Field or Lab	Field	Field	Lab	Field	Lab	Units
Density	1.6	1.9	1.6	1.2	1.2	Specific Gravity
5 Solids	26%	35%	17%	10%	7%	% by volume
Salt Conc.	71.2	89.1	75.0	17.0	17.0	kg/m ³
Salt Type	KCl	KCl	KCl	NaCl	NaCl	na
MBT ¹	44.1	23.2	21.5	99.7	71.2	kg/m ³
XC Polymer	2.1	2.0	1.3	—	—	kg/m ³
10 Starch	17.1	—	17.1	11.4	11.5	kg/m ³
Bentonite	—	14.0	—	80.0	71.2	kg/m ³
Polymers ²	2.0	4.0	2.0	1.0	1.0	kg/m ³
Dispersants	—	1.5	—	14.2	14.0	kg/m ³

Notes:

15 1. MBT represents Methylene Blue Equivalents (cation exchange capacity of the clays present in the drilling fluid). The MBT value is noted, with the bentonite which was reported as being added by the drilling fluid supplier, so as to calculate how much clay is of formation origin.

2. The polymers are from the polyacrylamides groups, and high temperature stable vinyl - copolymer groups; the dispersants noted are lignosulfonate and lignin resins.

20

TABLE 1

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Example 2 - Evaluation of salts and acids

The testing and evaluation consisted of determining, A)

which salts, within a selected solubility range were most

5 destructive and B) the most destructive and soluble acids
within a joint compatibility solubility range with the
salts.

Each filtercake was made and was fixed with an inert

10 fixative to the bottom of a petri dish to prevent
flotation. Into each, the test solution was added then
decanted using gentle suction, and fresh fluid added, at 10
minute intervals over 1 hour, with a determination of
results made at the end of that period.

15

The base line was determined from physical change in
filtercakes in independent testing of each salt and acid.
Then the same determination was made for the combination of
the two most compatible salts and acids.

20

The secondary selection criterion was evaluation of a
formulation's reaction with a formation (mud), versus
potential environmental impact of the spent resultant
product. The human safety factor was taken into account,
25 as the products were selected for testing based on human
working conditions and safety limitations, including effect
of disposal of used composition by release into the
environment.

30 Based on a series of evaluation points, the products,
individually, and in combination were graded on a 0 to 5
scale, as defined below:

0. No effect on filtercake.

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1. Mildly disruptive - disturbs surface of cake.
2. Disruptive, with generalized surface cracking and dehydration of cake.
3. Disruptive, with generalized cracking, localized fissures appear with blistering.
5. Disruptive, with severe cracking and blistering, associated with fissuring and uplifting of cake from plate bed.
4. Disruptive, with severe cracking, fissuring and lifting of filtercake from plate bed.

The relative concentrations of salts and acids used varied, but were uniformly stepped from 10 g/l upwards until near saturation of each individual component.

Table 2 lists the maximum concentrations of salts used to
15 achieve any or in some cases, a maximum effect.

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Series 1	Mud Type 1	Mud Type 2	Mud Type 3	Mud Type 4	Mud Type 5	Total
Sodium Chloride						
60 g/l	0	1	0	1	0	2
5 Calcium Chloride						
400 g/l	1	1	1	1	1	5
Magnesium Hexahydrate						
475 g/l	1	1	1	2	0	5
10 Potassium Chloride						
227 g/l	2	1	1	1	1	6
Sodium Thiosulphate						
Pentahydrate						
525 g/l	1	0	0	1	0	2
15 Sodium Acid						
Tetraphosphate						
175 g/l	1	1	1	1	1	5
Sodium Potassium						
Tetraphosphate						
225 g/l	1	1	0	1	0	3
20 Potassium Formate						
70% w/w	1	0	0	2	2	5
Cesium Formate						
50% w/w	0	0	0	1	1	2

TABLE 2

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The above results include only those salts tested which gave results of a total of 2 or higher. Calcium Bromide, and Zinc Bromides gave good results but did not meet the environmental criterion.

5 After evaluation of the best potential salt types, based on the criteria above, the remaining salts were mixed with numerous acids in various concentrations until a peak performance was noted. The results displayed in Table 3 are those obtained using citric acid. The raw acid was
10 added to the brine mixes in various concentrations as shown in Table 3.

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Series 2 Acid:Citric	Mud Type 1	Mud Type 2	Mud Type 3	Mud Type 4	Mud Type 5	Total
Sodium Chloride						
60 g/l, acid 300 g/l	2	2	1	1	1	7
5 Calcium Chloride						
400 g/l, acid 225 g/l	3	1	1	3	1	9
Magnesium Chloride Hexahydrate						
475 g/l, acid 315 g/l	2	2	1	3	2	10
10 Potassium Chloride						
227 g/l, acid 400 g/l	5	5	1	3	1	15
Sodium Thiosulphate Pentahydrate						
525 g/l, acid 135 g/l	1	1	1	1	1	5
15 Potassium Formate						
70% w/w, acid 105 g/l	3	1	1	3	2	10
Cesium Formate						
50% w/w, acid 75 g/l	2	1	1	2	1	7

TABLE 3

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The citric acid used was 99.9% citric acid monohydrate. The amounts added were dependent on solubility in the various brines. Other acids were tested in the same manner. The amounts of acids used were solubility related
5 to the brine test solutions in Series 1 (Table 1).

After the first series of evaluations, the acids were tested in small amounts, dissolved in fresh water, and the acid concentration increased in approximately 50 g/l increments until the maximum effect was noted. The salts
10 were then mixed into the acid solutions and tested as noted in the tests above against the same criterion. The results are given in Table 4, for potassium chloride.

- 20 -

Series 4 Salt:KCl	Mud Type 1	Mud Type 2	Mud Type 3	Mud Type 4	Mud Type 5	Total
Citric Acid						
400 g/l, salt 5 g/l	3	2	1	1	0	7
Citric Acid						
400 g/l, salt 55 g/l	3	2	1	1	0	7
Citric Acid						
400 g/l, salt 100 g/l	3	2	1	1	0	7
Citric Acid						
400 g/l, salt 150 g/l	4	3	1	2	1	11
Citric Acid						
400 g/l, salt 200 g/l	5	5	1	3	2	16
Citric Acid						
400 g/l, salt 250 g/l	5	5	1	3	2	16

15

TABLE 4

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The same procedure was repeated using all the various acids and salts noted. The citric acid gave the best results with potassium chloride. Citric acid/magnesium chloride 5 and phosphoric acid/potassium or magnesium chloride combinations were also very useful, but in the latter case, required very high concentrations of phosphoric acid (> 35% w/w).

10 With the results from Series 4 in hand, efforts concentrated on formulations containing citric acid monohydrate, and pure potassium chloride to obtain optimal economical concentrations. 5 to 2.5 gram increments were tested, and the ranges narrowed until no improvement was 15 noted.

The optimal ranges were extrapolated graphically as shown in Figure 1, from which it can be seen that over a range of concentrations centering about 217 g/l citric acid 20 and 225 g/l potassium chloride, maximum performance was achieved.

With the determination that excellent performance could be obtained on the removal of the polymer filtercakes, 25 efforts were concentrated on the additions of other acid and salt additives in an attempt to improve performance on the bentonite based muds.

It was found that sodium acid pyrophosphate (SAPP) in small 30 quantities, did marginally improve the performance of the citric acid/potassium chloride solution, and therefore this compound was added to the most preferred formulation, termed Formulation A hereinafter.

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Results obtained with Formulation A are given below in Test Series 12, Table 5.

217 g citric acid: 225 g potassium chloride: 19.5 g SAPP (100%), water to 11 = Formulation A

5

Series 12	Mud Type 1	Mud Type 2	Mud Type 3	Mud Type 4	Mud Type 5	Total
Formulation A	5	5	2	4	2	18

TABLE 5

Example 3 - Comparison of Formulation A with other free-pipe additives

10 Formulation A (example 2) was tested against a commonly used, commercially available free-pipe additive, hydrochloric acid (15% in CaCl_2 brine), and the next best test formulation, namely phosphoric acid (30% w/w) in KCl (20% w/w) as a control. In addition, acetic acid (35% in saturated CaCl_2 brine) was run. The free pipe additive used was Pipelax (manufactured by M.I. Drilling Fluids), blended with Diesel oil as per the suppliers recommended instructions.

The results are given in Table 6.

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Series 13	Mud Type	Total				
	1	2	3	4	5	
Formulation A	5	5	3	3	1	17
Pipelax	1	0	1	2	1	5
HCl + CaCl ₂	2	2	2	1	1	8
Acetic acid + CaCl ₂	2	3	1	2	0	8
Phosphoric Acid + KC1	3	3	1	1	0	8

TABLE 6

10 The results from Series 13 verified the theoretical and laboratory work done. Formulation A was superior by at least a factor of 100% over currently available products and additives.

15 This testing was repeated using numerous other criteria, with the same result.

Example 4

The final testing was to use Formulation A (Example 2) as a stimulation fluid to aid well clean-up. For this purpose, 1.5 cm thick sandstone cores were used.

The cores were cut longitudinally into sections designed to fit into a pressure chamber for imprinting filtercakes on cores to 2000 psi. The cores were flushed and cleaned with

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methanol and dried.

The cores were then inserted into the pressure chamber, and
a base line directional flow established where (B>W) was
5 the well bore to formation direction of flow, and (W>B) was
the return flow from the formation to the wellbore.

1. The base line permeability of each core plug was
established using North Sea Brent crude oil.
10 2. The core plugs were rewashed and dried.
3. A mud sample was placed over the core plug in the
core chamber, with a pressure of 1000 psi applied to
impregnate the core with filtrate, and build up a
filtercake on the borehole side of the coreplug.
15 (Mud filtrate B>W).
4. The pressure was released, and the drilling mud
replaced with the test solutions of 15%
hydrochloric acid or Formulation A.
5. The core was again pressured (B>W) to 1000 psi and
held for 15 minutes.
20 6. The core plug was then reversed pressurized using
crude oil from the chamber opposite the well bore
side (W), and the crude allowed to flow back in the
direction (W>B).
25

The results of these tests were repeated, and are tabulated
in Table 7.

Only muds 1 and 2 were tested, as most fields are drilled
30 using mud from previously drilled section, or with used
muds. Mud type 4, was not considered suitable, as
bentonite based fluids are not ideal for drilling
production reservoirs.

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Series 16-21

Average Results of Five Runs

		MUD 1	Base P	Return P	% Return	MUD 2	Base P	Return P	% Return
5	Formulation A		619	321.88	52.0%		605	320.65	53.0%
	15% HCL		621	242.19	39.0%		595	267.75	45.0%
	Formulation A		487	248.37	51.0%		488	253.76	52.0%
	15% HCL		519	241.41	39.0%		1278	472.86	37.0%
	Formulation A		596	327.8	55.0%		1156	658.92	57.0%
	15% HCL		589	229.71	39.0%		1149	413.64	36.0%
	Formulation A		877	420.96	48.0%		1189	630.17	53.0%
	15% HCL		596	274.16	46.0%		1016	396.24	39.0%
	Formulation A		988	474.24	48.0%		875	429.24	49.0%
	15% HCL		1012	414.92	41.0%		877	324.49	37.0%

Average Return Permeability

15	Formulation A	50.80%	52.80%
	15% HCL	40.80%	38.80%

Where Base P = Base permeability in mD; Return P = Return Permeability in mD.

TABLE 7

20 This series of tests demonstrated the clear superiority of Formulation A over the currently extensively used hydrochloric acid formula.

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Example 5

A preferred formulation of the composition is prepared as follows:

Potassium chloride (99% pure) 160 grams

5 Dissolve in water

Citric acid monohydrate 217 grams

Adjust volume to 1 litre with water

This composition is suitable for use in all the applications described above.

10 Tests were undertaken to assess the environmental impact of formulation A (example 2). The formulation was found to have low toxicity when measured on the standard marine test species *Acartia tonsa* and *Skeletonema costatum*, using the protocols adopted by PARCOM and the regulatory agencies in
15 the signatory governments (including MAFF in the U.K., SFT in Norway and the Inspectorate of Mines in the Netherlands). The formulation was found to be readily biodegradable (100% aerobic degradation in 5 days, as measured according to the OECD guideline 306 for the measurement of marine
20 degradability).

It will of course be understood that the invention is not limited to the specific details described herein, which are given by way of example only, and that various modifications and alterations are possible within the scope
25 of the invention as defined in the appended claims.

CLAIMS:

1. A composition effective to dissolve filtercake in a well bore, the composition comprising one or more water soluble organic acids in an aqueous solution of one or more of a salt selected from alkali metal chloride, alkali metal formate, acid tetraphosphate, alkaline earth chloride, alkali metal thiosulphate or the like.
- 10 2. A dry powder mixture for use in the preparation of an aqueous composition which is effective to dissolve filtercake in a well bore, the mixture comprising a salt of one or more water soluble organic acids and one or more of a salt selected from alkali metal chloride, alkali metal formate, acid tetraphosphate, alkaline earth chloride, alkali metal thiosulphate or the like.
- 15 3. The invention according to Claim 1 or Claim 2, in which the water soluble acid comprises 0.5% to 75% w/w of the composition, and preferably 10% to 35%.
- 20 4. The invention according to any of Claims 1 to 3, in which the salt comprises 0.5% to 75% w/w of the composition, and preferably 10% to 35%.
- 25 5. The invention according to any preceding claim, in which the water soluble organic acid is selected from the group comprising citric acid, oxalic acid, ascorbic acid, succinic acid, malonic acid, maleic acid and lactic acid, or any combination thereof, in any ratio.
- 30 6. The invention according to any preceding claim, in which the salt is selected from the group comprising potassium chloride, sodium chloride, magnesium chloride,

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sodium acid tetraphosphate, sodium thiosulphate pentahydrate, sodium formate, potassium formate and cesium formate, or any combination thereof, in any ratio.

5 7. The invention according to any preceding claim including an alkali metal pyrophosphate salt, preferably sodium acid pyrophosphate.

8. A composition according to any preceding claim
10 comprising 200 to 230g citric acid monohydrate and 200 to 235g potassium chloride per litre of water.

9. A composition according to claim 8, further comprising
15 to 25g sodium acid pyrophosphate per litre of water.

15 10. A composition according to any of Claims 1 to 9 for use as a filtercake dissolving additive in the drilling and maintenance of wells.

20 11. A composition according to any of Claims 1 to 9 for use as a fixer spacer in the drilling of wells.

12. A composition according to any of Claims 1 to 9 for use as a stimulating fluid for blocked or partially blocked
25 oil or gas wells.

13. A method of freeing stuck pipes in the drilling of well bores, the method comprising introducing a composition according to any of Claims 1 to 9 into the bore in the
30 region of the stuck pipe so as to dissolve and remove filtercake adhering to the pipe.

14. A method for securely fixing well casing pipe in a well bore, the method comprising introducing the

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composition according to any of Claims 1 to 9 into the space between the pipe and the bore walls, allowing the composition to dissolve filtercake from the said space and introducing a fixer compound to displace the composition
5 and dissolved filtercake residues.

15. A method for stimulating production from an oil or gas well, comprising introducing into the well an amount of the composition according to any of Claims 1 to 9 effective to unblock gas or oil supply pores by dissolving blocking
10 filtercake therefrom.

1/1

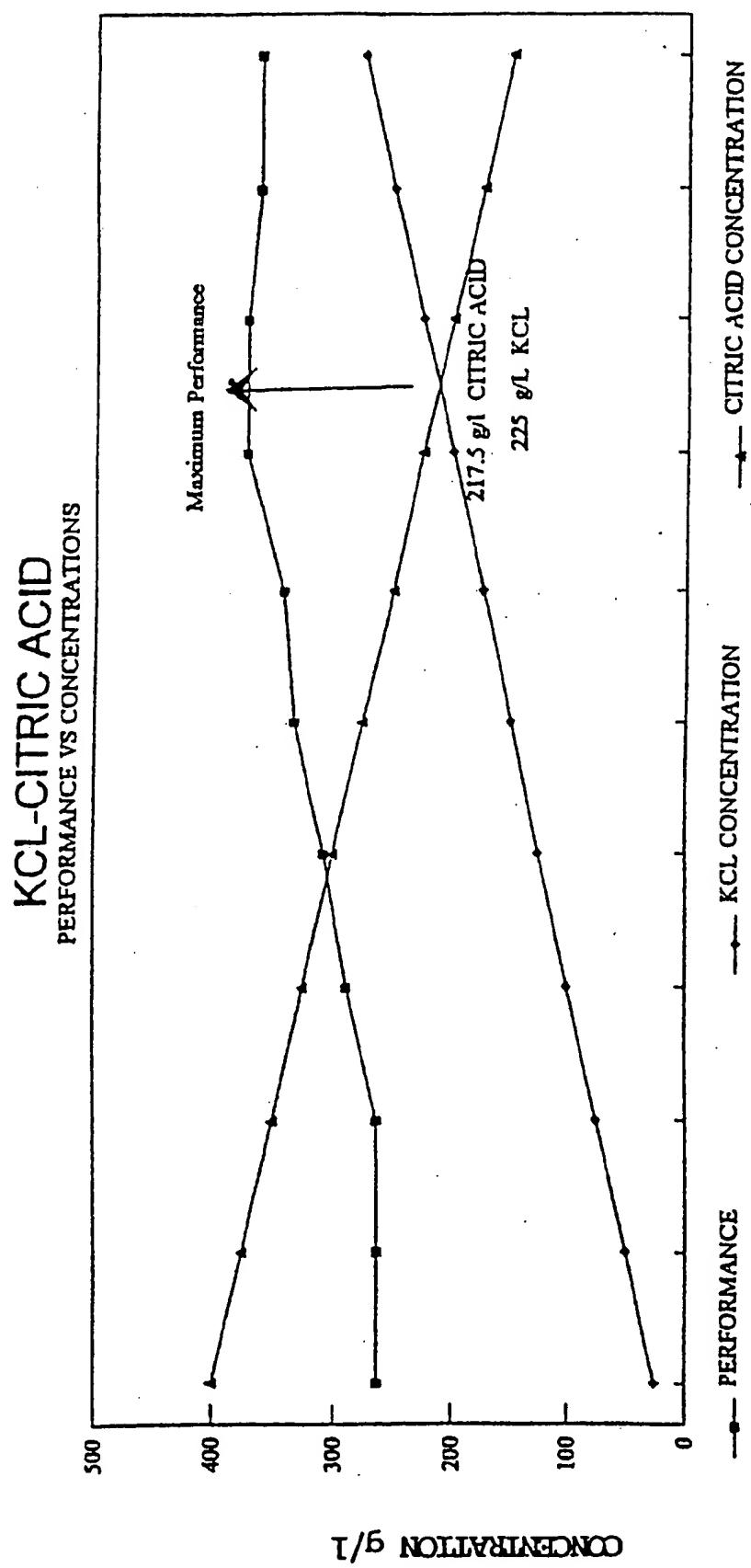


FIGURE 1

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No
PCT/EP 93/02346

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 E21B37/06 E21B43/25 E21B33/13

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 067 389 (J.G.SAVIUS) 10 January 1978 see claim 1 -----	1-15
A	US,A,3 135 325 (H.W.PARKER) 2 June 1964 see column 2, line 63 - column 3, line 21; claim 1 -----	1-15
A	EP,A,0 326 720 (ENIRICERCHE) 9 August 1989 see claims 1-14 -----	1-15

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *'A' document defining the general state of the art which is not considered to be of particular relevance
- *'E' earlier document but published on or after the international filing date
- *'L' document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *'O' document referring to an oral disclosure, use, exhibition or other means
- *'P' document published prior to the international filing date but later than the priority date claimed

- *'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *'&' document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 93/02346

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4067389	10-01-78	NONE		
US-A-3135325		NONE		
EP-A-0326720	09-08-89	AU-A-	2685588	10-08-89
		DE-A-	3872212	23-07-92
		JP-A-	1219289	01-09-89
		US-A-	4986356	22-01-91